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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

# GALVANIC POLARIZATION ON A MERCURY CATHODE.

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Presented by T. W. Richards. Received July 4, 1905.

OUR knowledge concerning the real mechanism of chemical reactions is very meagre, even in the case of those occurring in homogeneous systems. Still less do we know of what the processes really are that occur in or near the surface of discontinuity in the case of a heterogeneous system. To the latter class belong all electrolytic reactions, and here the phenomenon of galvanic polarization offers an especially promising field for investigation. Unfortunately, most studies in polarization have been made under conditions too complicated to permit a ready interpretation of their results. Even in cases where the polarization of a single electrode has been studied alone, the essential phenomenon has been frequently obscured by the presence of substances produced at the other electrode and the existence of secondary reactions due to other impurities, notably atmospheric oxygen. In cases also where slow diffusion processes occur, — such, for example, as a diffusion of gases into platinum,* — the previous history of the cell is an important and usually an unknown factor.

It has been our purpose in the present work to choose a single definite electrolytic reaction of a simple character, and, eliminating with the greatest care secondary reactions of all kinds, to study the polarization accompanying this reaction under varying conditions. The reaction chosen was the deposition of hydrogen from normal sulphuric acid upon a mercury cathode. In other words, we have studied the phenomenon known as the over-voltage (Ueberspannung) of hydrogen. Mercury was chosen for the cathode metal because of the high over-voltage upon it, because of its small capacity for absorbing hydrogen, because it is the only metal which is not liable to accidental variations in surface, and finally because we believed that with this metal, if with any, we would find evidence of the break in continuity (Knickpunkt) of the polarization curve, which has been described by numerous observers, but which has been attributed by others to erroneous observations or to incorrect interpretation of results.

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* See Cottrell, Zeit. phys. Chem., **42**, 385 (1903).

For measuring polarization two general methods have been employed. One consists in measuring directly the potential of the electrode in question against a standard electrode, either while the main current is passing or immediately after it is broken. The other method consists in measuring the total electromotive force between the two electrodes during the flow of a given current. The difference between this electromotive force and that which exists when an infinitely small current passes, may be called the total polarization, and is the sum of three terms: the polarization potentials at the two electrodes, and the fall of potential through the electrolyte. By diminishing the resistance in the electrolyte the latter term can be made negligibly small (except in case a resisting film forms at one of the electrodes). If, then, we use at one terminal an unpolarizable electrode, the total polarization is a measure of the polarization at the other electrode. This was the method adopted.

In order to exclude all side reactions, the liquid about the cathode must be carefully protected from any contamination by substances produced at the anode. This might be accomplished by separating the two electrodes so far as to prevent diffusion from one to the other during the time of the experiment. This would not only have necessitated a very complicated apparatus, but, by introducing a large resistance, would have prevented the simple calculation of the polarization at the cathode from the total polarization of the cell. It seemed better, therefore, to look for a suitable anode which could be used directly in the same liquid with the cathode without introducing any foreign substances into the electrolyte. The choice apparently lay between a lead peroxide electrode and an electrode of hydrogen upon platinized platinum. Since, as will be shown presently, the merest traces of impurity in the electrolyte may vitiate the results, it was feared that even the minute quantities of lead that would go into solution from the former electrode might be dangerous. We finally adopted, therefore, the hydrogen electrode in the usual form of a spiral of platinized platinum foil, half immersed in the electrolyte and bubbled over with hydrogen. It was not certain in advance that such an electrode could be regarded for our purpose as unpolarizable, but preliminary experiments indicated this to be the case for such small currents as were to be used. This conclusion was completely verified by our later experiments, as will be shown.

The electrolytic cell and the measuring apparatus are sketched in Figure 1. The cell consists of a glass bottle, which is immersed in a thermostat (the latter not shown in the figure). B represents the tube by which the hydrogen enters the cell; C is the platinum electrode, made of a strip of platinum foil of about thirty square centimeters, platinized with pure platinum chloride, carefully cleaned and treated for some time with boiling water, to remove any loose particles that might otherwise be disengaged by the hydrogen bubbles and carried to the cathode; E is the exit tube for the hydrogen; D is a tube two millimeters in internal diameter, containing mercury, constituting the cathode. In order to determine whether diffusion processes in the electrolyte play an important part in the phenomenon cited, it was our original purpose to vary the height of the mercury in D, and find the effect upon the magnitude of the current, at potentials insufficient to produce a bubble of hydrogen in the tube.* As a matter of fact, however, we found that after complete saturation of the electrolyte with hydrogen no potential

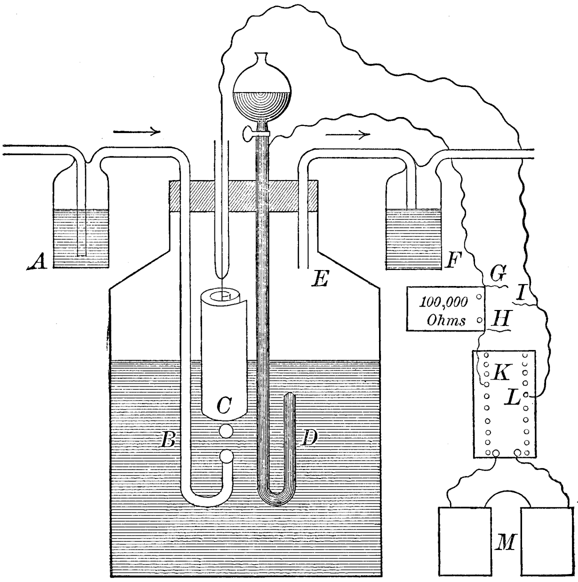

FIGURE 1.

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* Cf. Caspari, Zeit. phys. Chem., **30**, 89 (1899).

was too small to produce a bubble, which indeed appeared to form quantitatively according to Faraday's law. A current as low as $10^{-8}$ amperes, resulting from a potential of approximately .2 volt, gave a bubble visible to the naked eye within a minute, although the mass of this bubble must have been less than $10^{-11}$ grams. The apparatus, therefore, as a current detector, is almost as sensitive as a good galvanometer. On account of the formation of these bubbles it was found impracticable to experiment with the mercury below the end of the tube D, and in all our experiments the top of the mercury meniscus was kept at a level with the end of the tube.

The various tubes leading into the cell passed tightly through a rubber stopper. The use of rubber, although possibly objectionable, was decided upon in order to facilitate such alterations in the apparatus as the course of the experiments might make desirable. All possible precautions were taken to prevent the rubber from contaminating in any way the contents of the cell.

For preparing pure hydrogen a large generator with electrodes of zinc amalgam and copper, of the type first used by Cooke and Richards,* was employed. It was so arranged that the liquid could be withdrawn and new zinc and acid added without the entrance of a trace of air. The new acid, before it was introduced, was always treated for several days beforehand with a stream of hydrogen.

Before entering the cell the hydrogen passed through a wash-bottle A, containing sulphuric acid of the same strength as that in the cell, and on emerging it passed through a wash-bottle of mercury F, so that the pressure in the apparatus was always several centimeters of mercury above that of the atmosphere, thus preventing the leaking in of air.

The figure shows also the essential electrical connections. M represents a storage battery whose current passes through a resistance box of the form invented by Ostwald for measuring potentials. By moving the pegs L and K of this box a current of any desired strength could be tapped off to the cell, in circuit with which a resistance of 100,000 ohms was placed.

The two quantities to be measured were the potential between the electrodes and the current. The latter was obtained by measuring the potential fall in the 100,000 ohms' resistance. In other words the measurements consisted in finding the potentials between G and I, and between H and G. These were obtained by means of a potentiometer

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* Amer. Chem. Jour , **10**, 81 (1888).

(not shown in the figure) based on the Poggendorff method. In order to avoid changes in the polarization the potentials were first compensated as nearly as possible with a Lippmann electrometer, and then more exactly with a delicate galvanometer.

Since the internal resistance of the cell was low and the currents small, the fall of potential in the cell never amounted to more than a small fraction of a millivolt and could therefore be disregarded. Having then a cell with an unpolarizable hydrogen anode and zero fall of potential in the liquid, the total potential between the electrodes is a direct measure of the polarization of the cathode, for the whole process of the cell consists in hydrogen dissolving at the anode and forming again at the cathode, and the whole counter electromotive force of the cell is therefore merely a measure of the work lost in that irreversible process at the cathode which is responsible for the phenomenon of over-voltage.

The importance of using pure materials in this work is illustrated by the experiments of Walker and Paterson*. According to these authors, in the amalgam soda process where a solution of sodium chloride is electrolyzed with a mercury cathode, the presence of minute quantities of metallic impurities sometimes causes an enormous difference in the proportion between the amounts of sodium and hydrogen deposited. Thus, for example, the yield in sodium was lowered from 100 per cent to less than 70 per cent by one part in 10,000 of iron, cobalt, or nickel. In other words, the impurity in some way † assists enormously the formation of hydrogen from hydrogen-ion at the electrode, the very reaction with whose velocity we are concerned.

The sulphuric acid used in our experiments was prepared by the distillation of the best acid obtainable for analytic purposes. For preparing the mercury a new method was employed, which seems more trustworthy than any of those in common use. This method consists in heating mercuric oxide of high purity obtained in the wet way, and condensing the mercury set free. The oxides of such metals as zinc and cadmium are not decomposed by heat, while metals like platinum and silver will be set free but not volatilized. Mercury is the only readily volatile metal whose oxide is decomposed at red heat. For preparing small quantities of very pure mercury this method may, therefore, be recommended. In order to accelerate the decomposition and also to prevent the reunion of mercury and oxygen, the process is best carried on in vacuo.

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* Trans. Amer. Elec. Chem. Soc., **3**, 185 (1903).

† Mr. R. A. Hubbard has been kind enough to make a few experiments to verify the work of Walker and Paterson. He corroborates fully their main results and finds, as they did, that the formation of hydrogen at the cathode is associated with the formation of a scum on the mercury surface. In order to obtain some idea of its nature, the experiments were repeated in a weak acid solution. In this case the scum did not appear, nor was the yield of sodium appreciably affected by the impurities. It is probable, therefore, that the scum is due to the hydroxide of the metallic impurity and that it favors the formation of hydrogen in the same way that platinum favors its formation from zinc in the presence of acid, by lowering the over-voltage. Notwithstanding this evidence of the comparative harmlessness of metallic impurities in an acid solution, we have deemed it advisable to take all possible precautions to avoid impurities of every kind.

After the apparatus was set up and hydrogen had passed through the cell for several days to drive out the enclosed air, measurements were begun, but at first no constant results could be obtained. The current was subject not only to gradual changes but to sudden and capricious fluctuations, which rendered the experiments valueless. This unsatisfactory behavior, which may have been due to traces of oxygen clinging obstinately to the cell, or perhaps to incomplete saturation of the platinum electrode with hydrogen, continued for a surprisingly long time, and only after several weeks could definite and constant readings be obtained. Indeed, most of the results noted below were obtained after nearly three months, during which time hydrogen had been passing continuously through the cell at the rate of one cubic centimeter or more per hour. During this time also a current of about five-millionths of an ampere was sent through the cell continuously in order to precipitate any mercury which might have found its way into the solution and especially to help establish constant conditions at the cathode, partly by reducing the last traces of oxygen and partly by the mechanical stirring caused by the bubbles of hydrogen.

At first it seemed that these bubbles, which, as we have stated, were invariably formed by the current, might cause considerable inconvenience and uncertainty in the measurements. The bubble always started at the line of contact between the glass and mercury, but on becoming large enough to be easily visible to the eye it would mount suddenly to the top of the meniscus and there continue to grow, clinging to the mercury with great tenacity. The only easy way of removing the bubble was to tip the cell so as to bring the meniscus for the moment above the surface of the acid. Fortunately this treatment proved to have no effect whatever on the polarization, so that with a given potential the bubble could, as a rule, be allowed to form and be removed repeatedly without changing the current. Occasionally, however, this was not the case, and therefore, in most series of experiments the current at every potential was read both before and after removing the bubble.

As a test of the serviceableness of our apparatus, it was important to determine how quickly a constant current would be established after increasing the external electromotive force. The results not only were eminently satisfactory for our purpose, but gave evidence of a remarkable and unique phenomenon. In cases where polarization depends upon processes of diffusion either in the electrolyte or in the interior of the electrode, experiments have shown that the current falls gradually after any increase in the electromotive force and that it takes hours, days, or even weeks for the establishment of a constant condition. In such cases comparable results can be obtained only by reading the current always at a definite, arbitrarily chosen time after the change in electromotive force. In our present case we found that when the electromotive force was suddenly increased the current became constant in less than a minute, and that before reaching constancy the current was *rising* instead of falling. Thus, in a typical case the current at the end of one-fifth of a second was a few per cent below the final value, after a quarter of a minute only about half of one per cent below.

This unusual phenomenon could hardly be caused by the heating effect of the extremely small currents, and must be due either to the breaking down of some surface resistance or to the formation by the current of some substance which accelerates the electrolytic reaction, that is, to a kind of autocatalysis. We will presently describe another phenomenon closely connected with this one.

The constancy of the current with a given potential and the immediate attainment of this constancy, together with the fact that neither tipping the cell so as to bring a new portion of the hydrogen electrode under the electrolyte, nor suddenly bubbling hydrogen over the electrode, produced any change in the current, we regarded as convincing proofs that the hydrogen electrode was perfectly unpolarizable for the currents used.

The method of finding the relation between potential and current strength was to begin at a low potential and at the end of regular intervals of time to raise the potential step by step to the highest value desired, and then by similar stages to bring it back to a low potential. To illustrate, let us consider a particular case, in which the external electromotive force was changed every ten minutes, the current being observed at the end of this period both before and after removing the hydrogen bubble. The following table gives the potential in volts and the corresponding currents in millionths of a milliampere. When the potential of .652 volts was reached, the current began to fluctuate, and therefore, without taking any readings, the potential was immediately lowered and the series continued. The whole experiment was at 21.9° C.

| E | I | E | I | E | I |
|---|---|---|---|---|---|
| 0.314 | 69 | 0.582 | 3720 | 0.544 | 2250 |
| 0.436 | 444 | 0.597 | 4815 | 0.524 | 1690 |
| 0.477 | 815 | 0.652 | | 0.494 | 1220 |
| 0.498 | 1130 | 0.608 | 6290 | 0.474 | 910 |
| 0.522 | 1580 | 0.593 | 4920 | 0.424 | 490 |
| 0.546 | 2140 | 0.578 | 3700 | | |
| 0.564 | 2880 | 0.561 | 2950 | | |

It has been shown by Jahn and Shoenrock,* by Haber † and others, both theoretically and experimentally, that in many cases the potential is a linear function of the logarithm of the polarizing current. In Figure 2, therefore, we have plotted from the values given in the table the potential E in one direction, in the other the logarithms of the current I. The various values obtained from the table are represented by the points of the arrows whose direction upward or downward indicates whether the values were taken on the way up to the high potential or on the way back to the low. We see that the points obtained in the first part of the experiment fall very exactly upon a straight line whose equation is

$$E = A \log I + B, \qquad (1)$$

where $A$ and $B$ are constants. The points on the way back from the high potential lie in every case above this line.

The latter behavior is entirely unexpected. Many cases have been studied in which the current is diminished by previous high polarization of the electrode, and this is obviously due to the slow disappearance of the polarization. But we see that in our case the current at a low potential is increased by the previous passage of a larger current at a higher potential. If this phenomenon had been observed in a single instance only, we should have attributed it to chance errors, but it occurred regularly in all our experiments. It can only be explained by the assumption that the current itself produces, either some substance that catalyzes the electrolytic reaction, or some condition of the cathode surface which aids the reaction, and that this effect is increased by increasing the current and persists for some time when the current is diminished. This is the very conclusion to which we have already been led by the other phenomenon mentioned above. Whatever the true cause of these two phenomena may be, it is in all probability the same for both. According to the observations of Russ,* who investigated the reducing power of the electric current when a number of different solid metals were used as cathodes, the cathode occasionally became "active," that is to say, permitted with the same potential a much greater current to flow. This "activity" appeared to be produced by the current, and more rapidly the larger the current. While this is similar to the phenomenon we have noted, we might expect a solid metal to suffer occasional changes of surface, but it is hard to see how any peculiar condition could establish itself on a mercury surface and persist after the removal of its cause

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* Zeit. phys. Chem., **16**, 45 (1895).

† Ibid., **32**, 193 (1900).

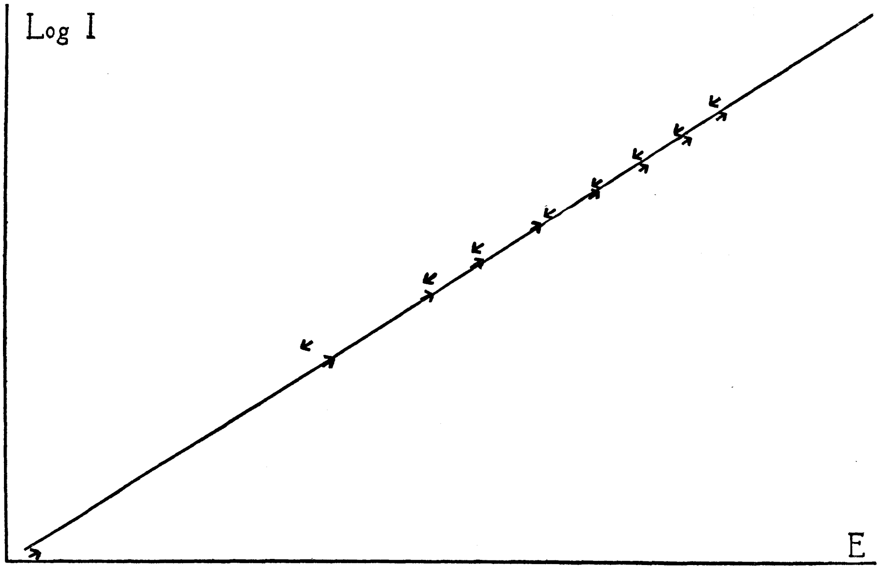

FIGURE 2.

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* Zeit. phys. Chem., **44**, 641 (1903).

and after standing and shaking, unless indeed it be due to the formation there of some new substance.

When we compare series of experiments conducted on different days and at different temperatures, ranging from 20° to 40°, we find that all give curves similar in every respect to the one shown in Figure 2. In every case the points obtained on the way up to the maximum potential lie on a straight line, while those obtained on the way down form an irregular curve lying above the line. Let us confine our attention to the former points and consider the theoretic grounds upon which the logarithmic formula is based. They are briefly as follows:

We assume that all true polarization (excepting the apparent polarization caused by an electric resistance at the electrode) is due to a counter-electromotive force caused either by the exhaustion of the substances used in the electrolytic reaction faster than they can be replaced, or by the accumulation of the products of this reaction faster than they can be removed. The degree of polarization is therefore a measure of the slowness of some irreversible process or processes, these being either processes of diffusion to or from the field of action (situated at or near the electrode surface), or chemical processes which supply the factors or destroy the products of the electrolytic action. From this point of view, the potential of the electrode, when the current is passing, differs from that of the unpolarized electrode by the potential of a concentration cell. From the Nernst equation, therefore, we are able to write for the potential of an electrode through which a current is passing the equation,

$$E = \frac{R\,T}{F} \ln \frac{c_1^{\frac{1}{n_1}} c_2^{\frac{1}{n_2}} \ldots}{c_1'^{\frac{1}{n'_1}} c_2'^{\frac{1}{n_2'}} \ldots} + \text{constant}, \qquad (2)$$

Where $c_1'$, $c_2'$, etc., represent the concentrations of the factors, $c_1$, etc., those of the products of the electrolytic reaction, $n_1'$, etc., and $n_1$, etc., are whole numbers, each of which represents the number of gram-equivalents in a gram-molecule of the substance in question.

Let us assume as a special case that the polarization is due solely to the accumulation of the products of the reaction. Let us further assume as a more special case that the polarization is due to the accumulation of only one of the products, and that the process by which this product is removed is a chemical one, obeying the law of Guldberg and Waage. Accordingly, equation (1) becomes

$$E = \frac{R\,T}{F} \ln c_1^{\frac{1}{n_1}}, \qquad (3)$$

while the velocity $V$ of the reaction is given by the equation, $V = k\,c_1{}^{m_1}$ where $m_1$ is the "order" of the reaction. The current can flow only as the reaction proceeds, and is therefore proportional to $V$. We may write therefore, $I = k'\,c_1{}^{m_1}$ whence $\ln\,c_1 = \ln I^{\frac{1}{m_1}} + \text{constant}$. Substituting in equation (3) we have,

$$E = \frac{R\,T}{m_1\,n_1\,F}\ln I + \text{constant},$$

or

$$E = \frac{.0002\ T}{m_1\,n_1}\log_{10} I + B. \tag{4}$$

Attempting to obtain a similar equation for the more general case, that two or more of the products are accumulated, we find that this is only possible when certain simple relations exist between the several values of $m$ and $n$.

One might consider from the development of equation (4) given by Haber (l. c.) that for all cases of polarization our accepted theories, without the aid of further hypotheses, would lead directly to an equation of the same logarithmic form. We see, however, that this is not the case. If the polarization be due to the exhaustion of one or more of the substances used up in the electrolytic reaction, the equation will take an entirely different form. We shall return to this point presently. But even assuming, as we did above, that the polarization is due to the accumulation of a single one of the products, we must introduce an important assumption in order to obtain equation (4), namely, that the substance is removed according to the simple law of Guldberg and Waage. This assumption includes two others, namely, that the process in question is a homogeneous chemical reaction, that is, that it includes no processes such as those of diffusion; and secondly, that the reverse reaction takes place to a negligible extent. The latter assumption is undoubtedly justified in most cases of the sort that we are considering, but whether the former assumption is justified can only be decided by experiment.

Equation (4) is more special and more definite than equation (1), for the former attempts to tell us more about the quantity $A$ than that it is a constant at a given temperature. Now, as a matter of fact, several investigators have shown that in a number of cases equation (1) holds with considerable accuracy, but that on the other hand, the values of $A$ not only cannot be calculated from equation (4), but are altogether inconsistent with it, $A$ proving in most cases to be greater than .0002 T, while the equation demands that it be either equal to this number or some simple fraction thereof, since $n$ and $m$ are always positive whole numbers by definition.

We can obtain the values of $A$ for the experiment whose results are given in Figure 2 by finding the slope of the straight line which best satisfies the individual points. This method permits a possible error of perhaps one per cent. The value so obtained is 0.159, if $E$ is expressed in volts. Similarly, from another experiment at the same temperature of 22° we obtain a value for $A$ of 0.157. The maximum value consistent with equation (4) is 0.058, when $m$ and $n$ are both equal to unity.

Between 35.5° and 36.5° four experiments were made. The values of $A$ obtained from these were 0.166, 0.157, 0.162, 0.166, with an average 0.163. The difference of over 3 per cent between this value and the average value, 0.158, found at 22°, is probably considerably greater than the error in determining these values, and shows that $A$ increases with the temperature; but whether proportionally to the temperature, as equation (4) demands, cannot be determined accurately from our experiments.

Since we find that our experiments are inconsistent with equation (4), we must conclude that at least one of the assumptions upon which that equation was based is false. The assumption which seems most likely to be erroneous is that the process determining polarization is a chemical reaction in a homogeneous phase. Even without the evidence of our experiments, is not this assumption improbable? * Is it not more probable that the processes, whatever they are, take place in that surface film which marks the transition from metal to electrolyte, and that processes of diffusion to, from, or through this film play an important rôle?

Two important diffusion processes suggest themselves at once as possible causes of the polarization, — the diffusion of gaseous hydrogen from, and the diffusion of hydrogen-ion to, the electrode. But these can both be excluded by the aid of certain general criteria.

If any polarization is due to the accumulation of the *final* products of electrolysis, there will be, as a rule, especially if this product is a gas, some potential at which its concentration becomes so great that a new phase will suddenly form and the current will begin to rise more rapidly. There will be, in other words, a break in continuity in the polarization curve. As a matter of fact, we observed no discontinuity, in the region of our experiments, that is up to over 0.7 volt, although at this potential, if the polarization were due to the accumulation of gaseous hydrogen, the hydrogen would be at a pressure of over $10^{24}$ atmospheres, — an inconceivable state of affairs. If further evidence were needed, the fact that no change in the current is observed, when the hydrogen bubble appears at the electrode, would show that the gaseous hydrogen plays no essential part in the phenomenon.

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* See Nernst, Zeit. phys. Chem., **47**, 52 (1904).

We can also show the unimportance of the diffusion of hydrogen-ion. Assume that the concentration of hydrogen-ion at a given distance from the electrode is kept constant by stirring or by convection, then, if the current depend on the diffusion of the hydrogen-ion, it would be proportional to the difference between that constant concentration and the concentration at the electrode. With the decrease of the latter this difference would approach constancy, and therefore our logarithmic formula would no longer hold. The current, instead of increasing more and more rapidly with increase of potential, would tend to assume a constant value. Brunner,* although recognizing this principle, holds to the view that the depletion of hydrogen-ion in the neighborhood of the electrode is responsible for the polarization, and he cites experiments to justify this view; but besides the evidence against this idea that we have presented, other entirely decisive arguments could be adduced; thus, for example, when hydrogen is deposited on certain metals, like platinum and iron, the polarization is not destroyed by thoroughly washing the electrode, and only disappears after the lapse of hours or days. It is obvious that the diffusion of hydrogen-ion can have nothing to do with this phenomenon.

One might ask with some reason whether it is possible that the process consists wholly or in part in a process of diffusion, since we have seen that a stationary condition is established almost instantly, when the external electromotive force is applied, while diffusion processes ordinarily reach a stationary condition only after considerable time. The answer must be that, if any part of the polarization is due to a process of diffusion, this diffusion must occur through a film of extremely small thickness. We may add that, since the diffusion must be slow in order to account for the polarization, either the film must present a very high resistance to the diffusion, or the diffusing substance must be at an extremely low concentration.

We have, then, reason to believe that the process responsible for polarization is not a homogeneous reaction, nor a process of diffusion through any considerable distance.

The theory of over-voltage, with which the authors began these experiments, was as follows: The reaction, $2\overset{+}{H} + 2\,\Theta = H_2$, does not occur in a single stage, but in the two following: $\overset{+}{H} + \Theta = H$, and $2\,H = H_2$. The reaction whose slowness causes the polarization is the second of these. In other words, the potential of a hydrogen electrode depends on the concentration of monatomic hydrogen, and this concentration increases rapidly during cathodic polarization on account of the slowness of the reaction by which it is removed. For example, at a polarization potential of 0.7 volt the concentration of this substance at the electrode would be $10^{12}$ times as great as it would be when in equilibrium with ordinary hydrogen. Nevertheless, both of these concentrations might be absolutely very small, and probably are. The difference in polarization with different cathodes would be explained by the different catalytic action of the material at the electrode, the polarization being less the greater the catalysis. This theory, although it has been suggested by Tafel,[*] has otherwise had no place in the numerous discussions which the phenomenon of over-voltage has occasioned. It possesses, nevertheless, a good deal of plausibility. We may in fact cause the electrolytic reaction to proceed in the very two stages which we have written above. When hydrogen is deposited on a palladium cathode, the hydrogen, forming without marked polarization, is absorbed by the metal, where it has been shown by two independent methods [†] to exist in the monatomic condition. If the hydrogen is then withdrawn from the palladium, it appears in the form of ordinary hydrogen, $H_2$.

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* Zeit. phys. Chem., **47**, 56 (1904).

But we have more striking arguments in favor of this theory. Those metals, notably platinum and palladium, in whose presence the electrolytic deposition of hydrogen and the reverse reaction, the electrolytic solution of hydrogen, progress most readily, are the very ones which we have every reason to believe catalyze the reaction $2H \rightleftarrows H_2$ (of course, if in one direction, in both). This reaction is doubtless a very slow one under most conditions. Hydrogen at ordinary temperatures is a pretty inert substance, but in the presence of palladium or platinum black it readily reduces a large number of substances. So also these metals aid the union of hydrogen with other elements, such as oxygen and the halogens. Furthermore, in every known case where hydrogen is produced by a reaction, the reaction is catalyzed by these metals. We may mention the action of metals on acids, the reduction of water by chromous salts, the decomposition of a solution of sodium in liquid ammonia.* It is possible that each of these reactions is catalyzed in a specific way; but it is much easier to believe that in every case the metal simply catalyzes the slow reaction, $2H \leftrightarrows H_2$, and that this is also the explanation of the electrolytic reaction that we are considering. It is to be noted that metals like mercury and lead, on which the over-voltage is highest, — that is, which are the poorest catalyzers of the electrolytic reaction, — have little influence on any of the reactions mentioned above.

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[*] Zeit. phys. Chem., **34**, 200 (1900).

[†] Hoitsema, Zeit. phys. Chem., **17**, 1 (1895). Winkelmann, Ann. der Phys., (4), **6**, 104 (1901).

Although we have laid stress upon the *a priori* plausibility of this explanation, we are nevertheless forced to admit that, while our experiments are in no way opposed to the theory, they fail at the same time to give any evidence in its favor, except in as far as they enable us to exclude certain other explanations and thus limit the field of possibilities. If the main reaction at the basis of polarization is the formation of ordinary hydrogen from monatomic, then our experiments only show that this reaction does not occur in a single homogeneous phase. Since in all probability the monatomic hydrogen is present in extremely small concentration, this would account for the slowness of any diffusion process in which it enters, even if the diffusion were through a thin film.

Let us return to our experimental results. We have seen that they may be represented by a number of almost parallel straight lines, whose equations are of the type $E = A \log I + B$. Let us now consider the quantity $B$.

While the cell gave consistent and constant results during the time required for a single series of experiments, there was some variation from day to day, so that the results of two different days gave, when plotted, two parallel but not always coincident lines. That is to say, the value of $B$ was not found to be constant, but for some unknown reason varied irregularly with the time.†

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* The interesting fact that this latter reaction is greatly accelerated by platinum was brought to our notice by Dr. C. A. Kraus.

† It is not impossible that this variation might have been due to changes in the barometric pressure, for, while small changes of pressure have no appreciable effect upon the potential of the reversible hydrogen electrode, they may have a considerable effect upon the velocity of the irreversible process, which is responsible for polarization. In fact, this is rendered highly probable by the experiments of Tammann and Nernst (Zeit. phys. Chem., **9**, 1, (1892)), who showed the great retarding influence of pressure on the reactions between metals and acids. Since in these reactions the only common feature is the formation of gaseous hydrogen from hydrogen-ion, it is probable that this is the reaction that the pressure retards. It is our intention in the near future to study especially the influence of pressure on the polarization of hydrogen.

Regarding the various straight lines as practically parallel within the range of our experiments, and giving to $A$ its average value, we may express all our results approximately by the equation $E = .0160 \log_{10} I + B$, where $B$ varies between the extreme values 0.014 and 0.069, $E$ being given in volts and $I$ in millionths of a milliampere.

On account of the temporal changes in $B$ it was difficult to find how this quantity changed with the temperature, for the values obtained on different days at different temperatures differed hardly more from one another than those obtained on different days at the same temperature. Attempts to solve this problem by suddenly changing the temperature back and forth failed because we found that after a change of temperature several hours at least were necessary for the establishment of constant conditions. The effect of temperature on the polarization cannot be large, and on the whole our experiments indicate, if anything, that at a given potential the current is smaller the higher the temperature.

This result appears at first sight opposed to the general law that the velocity of physico-chemical reactions increases rapidly with the temperature, but it must be borne in mind that this law holds only for given concentrations of the reacting substances, while, when the potential is kept constant and the temperature raised, the concentrations of the reacting substances may diminish very considerably.

We have not yet mentioned an interesting phenomenon which appeared when the potential was carried much higher than 0.7 volt. At these high potentials the current would frequently begin to fluctuate, and at the same type the hydrogen, instead of making a single bubble at the top of the mercury meniscus, would form a number of small bubbles which appeared not only at the surface of the mercury but also between the mercury and the tube, sometimes as much as a centimeter below the surface. This is not such a break in the polarization curve as we have mentioned above, which would indicate the sudden formation of some new product of the electrolysis, for it is not associated with a sudden rise in the current, but on the contrary usually brought the current down to an abnormally low value.

Probably this phenomenon is due to changes in the surface tension of the mercury produced by the high polarization, but it might be explained by the formation of an unstable amalgam of hydrogen, and this hypothesis should not be discarded until further experiments have been made.

It will be seen that the experiments which we have described in this paper have presented a number of new problems rather than solved the old, and they must therefore be regarded as preliminary to a more thorough investigation. Since, however, circumstances prevent a continuation of our work at this time, we publish the results so far obtained.

## SUMMARY.

The polarization observed when hydrogen is deposited electrolytically upon a mercury cathode is studied, the apparatus being designed to exclude as fully as possible all impurities and all side-reactions.

The polarization curve up to 0.7 volt is regular and shows no break in continuity. The relation between potential $E$ and current $I$ is given very exactly by the equation $E = A \log I \times B$ where $A$ and $B$ are constants.

The theory of this logarithmic equation is discussed.

It is shown that the polarization cannot be due to the slowness of diffusion either of hydrogen-ion to the electrode or of the hydrogen away from the electrode, but must be due to some intermediate reaction.

A theory is proposed concerning the nature of this reaction.

The effect of temperature on the polarization is considered.

Certain unexpected phenomena accompanying the polarization are discussed.